The role of vibrational–rotational coupling in V–V and V–R,T energy transfer[a),b)]

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The effect of neglecting vibrational–rotational coupling in energy transfer calculations is studied for collisions of HF ($v = 1 - 7$) with HF ($v = 0$). An analog of a "classical path" method is considered in which rigid-rotor trajectories are used to determine a time-dependent forcing term on the vibrational motion of each molecule. The results are compared with our quasiclassical calculations in which no such approximation was used. At higher vibrational states the rigid-rotor forced-oscillator model is found to predict substantially smaller V–R,T rate constants than those found in the exact study.

I. INTRODUCTION

The theoretical study of vibrational energy transfer in molecular collisions has long been of interest in chemical kinetics. A survey of the historical development of such calculations is given in Refs. 1 and 2.

Numerically exact quantum mechanical calculations of vibration-to-vibration (V–V) energy transfer have been restricted to a collinear geometry[3–6] due to the large increase in size (and expense) of the computation when rotational states are included. There have been extensive studies in developing various approximate methods in energy transfer calculations in order to treat problems of higher dimensionality. These methods include quasiclassical,[7] j_z-conserving coupled states approximation[8,9] and, for vibrational energy transfer, a classical path method.[10–17]

The classical path method involves treating one type of motion quantum mechanically (the vibrations, in the case of Refs. 10–17) and the remaining degrees of freedom using classical mechanics. A classical path method has been used very frequently,[18–24] usually to calculate electronic transition probabilities.

In this paper, the effect of vibrational–rotational coupling, and its omission in the classical path method, is examined for the system HF($v=1-7$) + HF($v=0$). For this purpose the quasiclassical analog of the classical path calculations is studied and the results are compared to our previous quasiclassical calculations in which the vibrational–rotational coupling is included.[25] The differences in results of the two quasiclassical calculations give an indication of the appropriateness of the classical path method in this application, an application where vibration-to-rotation-plus-translation was found to be very important.[25]

II. DETAILS OF CALCULATION

In classical path calculations[10–17] for vibrational–rotational–translational energy transfer calculations all of the degrees-of-freedom except the vibrations have been modeled by use of rigid-rotor classical trajectories. The rigid-rotor trajectories were used to determine a time-dependent driving force on the vibrational motion of each molecule. The time-dependent Schrödinger equation was integrated for the forced-oscillator motion. Both atom–diatom and diatom–diatom collisions were treated.[10–17] We consider here the diatom–diatom collisions where both vibration-to-vibration (V–V) and vibration-to-rotation, translation (V–R, T) energy transfer are possible.

To derive the equations that are the quasiclassical analog to the classical path treatment, we begin by writing the classical Hamiltonian for the diatom–diatom collision;

$$H = (p_1^2/2\,\mu_1) + (L_1^2/2\,\mu r_1^2) + V_{\text{vib}}(r_1) + (p_2^2/2\mu_1) + (L_2^2/2\,\mu_2 r_2^2) + V_{\text{vib}}(r_2) + \text{KE}_{\text{rel}} + V_{\text{int}}\,, \tag{1}$$

where p_i, μ_i, L_i, r_i, and $V_{\text{vib}}(r_i)$ are the radial momentum, reduced mass, rotational angular momentum, internuclear separation, and vibrational potential energy of molecule i, KE_{rel} is the kinetic energy of the relative motion of the two molecules, and V_{int} is the intermolecular potential energy. Hamilton's equations for the vibrational motion of molecule i are ($i=1,2$)

$$\dot{r}_i = p_i/\mu_i\,, \tag{2}$$

$$\dot{p}_i = \frac{L_i^2}{2\mu_i r_i^3} - \frac{\partial[V_{\text{vib}}(r_i) + V_{\text{int}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R})]}{\partial r_i}\,, \tag{3}$$

where $\mathbf{R}$ is a vector between the center of mass of each molecule; $\mathbf{r}_i$ is that for the axis of molecule i. The final term in Eq. (3) is the "driving force" experienced by the oscillator. In order to construct the quasiclassical analog of the classical path procedure of Refs. 10–17 we first calculate all the variables in Eqs. (2) and (3) except r_1, p_1, r_2, and p_2 as a function of time from rigid-rotor trajectories. The vibrational equations of motion for each molecule, Eqs. (2) and (3), are then integrated and the net change in vibrational state during each collision due to the driving force is determined. A Monte Carlo average is performed over a Boltzmann distribution of trajectory initial conditions. For comparison with the

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TABLE I. Rate constants[a] for rigid-rotor forced-oscillator calculation.

System[b]	k_{tot}[c]	k_{V-V}	$k_{V-R,T}$
1–0	−0.5 (0.3)[d]	•••	−0.5 (0.3)
2–0	25 (5)	23 (5)	1.2 (0.5)
3–0	35 (8)	32 (8)	2.1 (1)
4–0	67 (24)	62 (24)	5 (5)
5–0	51 (15)	42 (14)	9 (2)
6–0	89 (28)	19 (6)	70 (26)
7–0	115 (22)	20 (8)	95 (21)

[a]All rate constants in units of 10^{-12} cm^3 molecule^{-1} sec^{-1}.
[b]HF($v=1$ to 7)+HF(0), potential energy surface from Ref. 15, 300 K.
[c]$k_{V-V}+k_{V-R,T}$.
[d]Number in parenthesis is "one standard error," but see text concerning fluctuations.

exact trajectory results a cross-correlation method of analysis[26] is again used to calculate V–V and V–R, T rate constants from trajectory energy transfer data.

For the present system, HF($v=1$–7) colliding with HF($v=0$) at 300 K, the intermolecular potential energy surface used is that given by Poulsen *et al.*[15] and the vibrational potential is taken to be a Morse potential.[26] The present "right-rotor forced-oscillator" calculations are then compared with our earlier quasiclassical results.[25]

III. RESULTS AND DISCUSSION

The results of the present rigid-rotor forced-oscillator calculations are presented in Table I. They may be compared with our previous quasiclassical results,[25] given in Table II. The theoretical V–V rate constants in the two sets of calculations are seen to be in moderate agreement, the large numerical uncertainties notwithstanding. Despite the fact that on the average 700 trajectories were calculated for each of the seven systems studied, the numerical uncertainties (especially for the V–V rate constants) are rather large, because of large fluctuations from trajectory to trajectory that are not adequately described by the usual Gaussian distribution curve. One should probably calculate at least two or three times as many trajectories to obtain converged rate constants. However, in order to make as many comparisons as possible, a smaller number of trajectories was used.

TABLE II. Rate constants[a] for quasiclassical calculation.[b]

System[c]	k_{tot}[d]	k_{V-V}	$k_{V-R,T}$
1–0	0.2 (0.1)[e]	•••	0.2 (0.1)
2–0	19 (3)	17 (3)	1.7 (0.5)
3–0	28 (4)	24 (4)	4 (1)
4–0	53 (10)	31 (7)	22 (5)
5–0	69 (10)	9 (3)	60 (10)
6–0	156 (18)	14 (3)	142 (16)
7–0	455 (49)	17 (6)	438 (48)

[a]All rate constants in units of 10^{-10} cm^3 molecule^{-1} sec^{-1}.
[b]Reference 25 (includes vibration–rotation coupling).
[c]See footnote b, Table I.
[d]$k_{V-V}+k_{V-R,T}$.
[e]Number in parenthesis is "one standard error," but see text concerning fluctuations.

TABLE III. Correlation coefficients for changes in dynamical variables for HF($v_1=1$–7)+HF($v_2=0$) system.

		Correlation coefficient[a]		
X	Y	$v_1=1$	$v_1=4$	$v_1=7$
Δv_1	Δv_2	−0.99 (−0.99)[b]	−0.93 (−0.83)	−0.40 (−0.24)
Δv_1	ΔJ_1^2	−0.02 (−0.20)	−0.02 (−0.32)	0.08 (−0.80)
Δv_1	ΔJ_2^2	−0.16 (0.01)	−0.11 (−0.30)	0.01 (−0.64)
Δv_2	ΔJ_2^2	0.17 (−0.01)	0.15 (0.01)	0.18 (0.00)
Δv_2	ΔJ_1^2	0.02 (0.20)	0.05 (−0.03)	−0.02 (0.03)
ΔJ_1^2	ΔJ_2^2	−0.50 (−0.44)	−0.45 (0.09)	−0.56 (0.21)
Δv_1	ΔE_{tr}	−0.05 (−0.03)	−0.05 (−0.17)	0.05 (−0.48)

[a]See Eq. (4).
[b]For comparison, results from previous quasiclassical calculations in Ref. 25 are given in parentheses.

A systematic difference between the two sets of calculations is seen in the total deactivation and V–R, T rate constants. As the initial vibrational state of the excited HF increases, the rigid-rotor forced-oscillator model increasingly underestimates the amount of V–R, T energy transfer as compared to the more exact calculation.[25] This result is quite reasonable. In the forced-oscillator calculations the rigid-rotor trajectories are independent of the vibrational motion, and so one would not expect the correlation of vibrational and rotational changes to be correctly described.

Another illustration of the differences in the two sets of calculations is seen in the correlation coefficients for changes in dynamical variables. The correlation coefficient is a measure of the extent to which two variables x and y are correlated, and is calculated by

$$r=\frac{[\sum_i(x_i-\bar{x})(y_i-\bar{y})]}{[\sum_i(x_i-\bar{x})^2][\sum_i(y_i-\bar{y})^2]}\,. \tag{4}$$

The correlation coefficient can range between −1 and 1 for a perfect negative or positive linear correlation, respectively. If $r=0$ there is no linear correlation.

Correlation coefficients for the present calculations and for our previous quasiclassical study[25] are given in Table III. The most dramatic differences between those of Ref. 25 (given in parentheses) and the present ones are in the correlation of Δv_1 with ΔJ_1^2 and with ΔJ_2^2, at high v. The results of Ref. 25 showed very strong correlations in these cases, an indication of the importance of V–R, T transitions. However, in the present rigid-rotor forced-oscillator calculations these strong negative correlations are not seen, due to the neglect of the vibrational–rotational coupling.

IV. CONCLUSIONS

We found elsewhere[25] that vibration-to-rotation, translation transitions were particularly important at large v for this system. The neglect of vibrational–rotational coupling in the current "forced-oscillator" calculation has been shown to lead to significant underestimation of the total deactivation and V–R,T energy transfer rate

constants at large v. A major feature in the model is that the rotational motion is unaffected by changes in vibrational state during the collision. Therefore, it is expected that the large V–R, T transition probabilities would be predicted less accurately in this case.

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